involves a free-radical reaction, as previously suggested,[1,3] for which the preceding mechanism is represented.

Experimental[5]

Experiments with ultraviolet light were conducted in an apparatus similar to the one described by de Mayo[6] with slight modifications. The radiation sources for the acetone-initiated reactions and the direct light-induced reactions were accomplished by Hanau Q81 high pressure mercury vapor lamps fitted into Pyrex or quartz immersion tubes, respectively. The reaction mixtures were cooled externally by running water and were kept under oxygen-free nitrogen. Reactions in sunlight were performed in Pyrex tubes, and the system was flushed with nitrogen after each addition of the olefin.

Reagents were tetrahydrofuran, B.D.H., and tetrahydropyran and dioxane, Fluka. These cyclic ethers were freshly distilled over sodium before use: acetone, absolute, and 1-octene, Fluka. The olefin was shaken with aqueous ferrous sulfate solution and dried (Na_2SO_4); it was freshly distilled and filtered through a short column of Alcoa activated alumina F20 before use.

1-Octene and Tetrahydrofuran with Ultraviolet Light.—A mixture of 1-octene (0.5 g.), tetrahydrofuran (90 ml.), and acetone (5 ml.) was irradiated for 1 hr. A solution of 1-octene (5.1 g.) in acetone (5 ml.) then was added in ten equal portions in 1-hr. intervals and irradiation was continued for another 12 hr. Excess reagents were removed under reduced pressure and then the residue, whose infrared spectrum indicated only traces of carbonylic substances, was distilled. The fraction with b.p. 80–140° (1.5 mm.), 5.4 g., was chromatographed on alumina (270 g.). Elution with pentane gave 2-octyltetrahydrofuran (2.3 g., 25% based on olefin employed) which upon redistillation indicated b.p. 69–71° (0.4 mm.), $n^{26}\mathrm{D}$ 1.4410; lit.[7] b.p. 85–87° (3 mm.), $n^{20}\mathrm{D}$ 1.4412. This substance showed identical boiling point, infrared spectrum, refractive index, and gas chromatographic retention time with those of an authentic sample.[8] The n.m.r. spectrum of this compound exhibited multiplets at τ 6.15 and 8.1, a broad singlet at τ 8.65, and a triplet at τ 9.1 in the ratio 3:3.8:14:3.3.

Anal. Calcd. for $C_{12}H_{24}O$: C, 78.19; H, 13.13. Found: C, 77.90; H, 13.00.

1-Octene and Tetrahydrofuran in Sunlight.—A mixture of 1-octene (0.5 g.), tetrahydrofuran (90 ml.), and acetone (5 ml.) was left in direct sunlight for 1 day. A solution of 1-octene (5.1 g.) in acetone (5 ml.) was then added in ten equal portions in 1-day intervals, and the mixture was left in sunlight for another 7 days. After removal of the solvent, the residue, whose infrared spectrum indicated only traces of carbonylic substances, was filtered through alumina (450 g.) using a 1:1 benzene–ether mixture. The resulting oily residue (8 g.) was distilled *in vacuo*. The fraction with b.p. 70–130° (0.5 mm.), 5.5 g., was chromatographed on alumina (270 g.). Pentane eluted 2-octyltetrahydrofuran (2.7 g., 30%).

1-Octene and Tetrahydropyran with Ultraviolet Light.—The quantities and experimental conditions described above were followed. After removal of the reagents, the residue which contained only traces of carbonylic materials was distilled. The fraction with b.p. 75–150° (1.5 mm.), 4.3 g., was chromatographed on alumina (220 g.). Elution with pentane gave 2-octyltetrahydropyran (1.7 g., 17%), b.p. 84–86° (0.6 mm.), $n^{25}\mathrm{D}$ 1.4458. This substance showed the same physical properties as an authentic sample prepared by the method of Paul.[9] Its n.m.r. spectrum indicated multiplets at τ 6.0 and 6.65, a broad singlet at τ 8.65, and a triplet at τ 9.15 in the ratio 1:2:19.8:3.1.

Anal. Calcd. for $C_{13}H_{26}O$: C, 78.72; H, 13.21. Found: C, 78.26; H, 13.12.

1-Octene and Tetrahydropyran in Sunlight.—The procedure described above with the same quantities were followed. After the usual work-up, the remaining residue (7.1 g.) was distilled and the fraction with b.p. 75–150° (1.5 mm.), 3.3 g., was chromatographed on alumina (170 g.). Elution with pentane led to 2-octyltetrahydropyran (2.1 g., 21%).

1-Octene and 1,4-Dioxane with Ultraviolet Light.—Similar procedure and quantities as described above were followed. The residue which contained only traces of carbonylic substances was distilled and the fraction with b.p. 80–180° (0.5 mm.), 5.2 g., was crystallized from petroleum ether (b.p. 60–80°). The precipitate which consisted of the dimers of dioxane[10] was filtered and the mother liquor was chromatographed on alumina (250 g.). The oily substance obtained on elution with pentane was crystallized from pentane to give octyl-1,4-dioxane[2] (2.7 g., 27%), m.p. 37–38°. This substance was further characterized by its n.m.r. spectrum which showed a multiplet at τ 6.2, a broad singlet at τ 8.65, and a triplet at τ 9.1 in the ratio 7:14:2.9, as well as by its mass spectral analysis which indicated a parent ion with $m/e = 200$ and a base peak with $m/e = 87$.

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 72.46; H, 11.82.

1-Octene and 1,4-Dioxane in Sunlight.—The procedure described above, using similar quantities, was followed. After removal of the reagents, the residue was distilled and the fraction with b.p. 80–180° (0.5 mm.), 7.3 g., was collected. Dimers of dioxane were isolated as explained above, and the remaining residue was chromatographed on alumina (350 g.). Elution with pentane led to octyl-1,4-dioxane (3.4 g., 34%).

1-Octene and 1,4-Dioxane with Ultraviolet Light (without Acetone).—A solution of 1-octene (1 g.) in 1,4-dioxane (100 ml.) was irradiated for 1 hr. 1-Octene (4.6 g.) then was added in eight equal portions in 1-hr. intervals and the mixture was irradiated for another 12 hr. After work-up, octyl-1,4-dioxane (0.5 g., 5%) was obtained.

Acknowledgment.—The authors are grateful to Professor Franz Sondheimer for his interest and encouragement. We are also indebted to Dr. Shvo for the n.m.r. determinations and to Drs. W. A. Ayer and S. Wolfe for the mass spectral analysis.

---

(5) Boiling points and melting points are uncorrected. Merck "acid-washed" alumina was used for chromatography. Gas–liquid chromatography was carried out with a "Pye" argon instrument on a 10% Apiezon M-Celite column at 125°. The n.m.r. spectra were determined on a Varian A-60 spectrometer in deuteriochloroform using tetramethylsilane as internal standard. Analyses were carried out in our microanalytical section directed by Mr. R. Heller.

(6) P. de Mayo, "Advances in Organic Chemistry," Vol. 2, R. A. Raphael, E. C. Taylor, and H. Wynberg, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p. 370.

(7) G. I. Nikishin and V. D. Vorob'ev, *Izv. Akad. Nauk SSSR, Otd. Khim Nauk*, 892 (1962); *Chem. Abstr.*, **57**, 12,300 (1962).

(8) 2-Octyltetrahydrofuran was prepared by treating 2-furfuraldehyde with heptylmagnesium bromide followed by catalytic hydrogenation, chrominum trioxide oxidation, and Wolff–Kishner reduction.

(9) R. Paul, *Bull. soc. chim. France*, [5]**2**, 311 (1935).

(10) K. Pfordte, *Ann.*, **625**, 30 (1959); G. Sosnovsky, *J. Org. Chem.*, **28**, 2934 (1963).

Reactions of Acetylenes. III. Cyclization of Urethanes

Donald R. Cassady and Nelson R. Easton

Chemical Research Division, Lilly Research Laboratories,
Indianapolis 6, Indiana

Received February 21, 1964

Earlier work[1] in this laboratory and elsewhere has shown that *t*-ethynylcarbinols react with isocyanates to form urethanes (I) which can be readily converted to oxazolidinones (II) by treatment with sodium ethoxide.

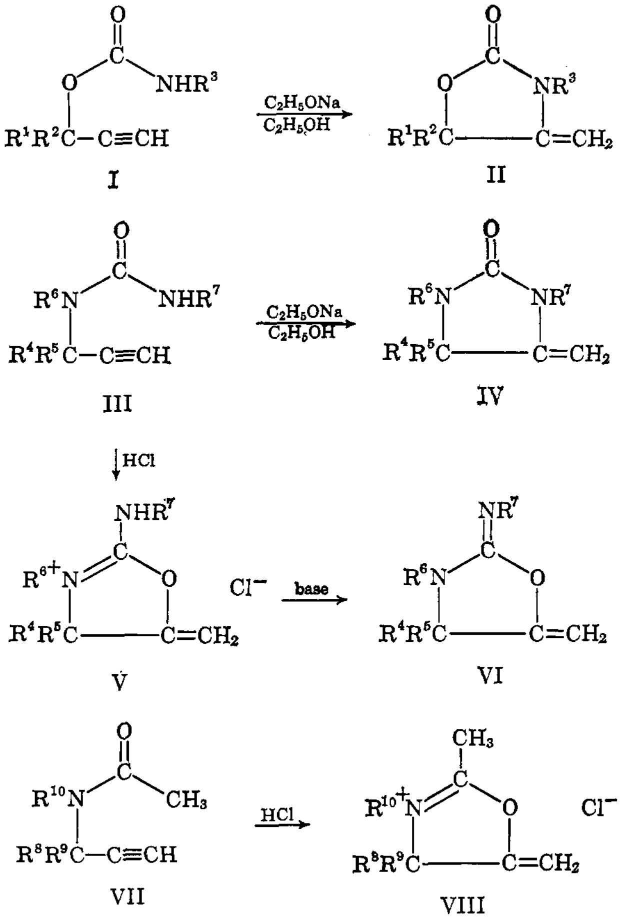
α,α-Disubstituted propargylureas (III) when treated with sodium ethoxide in ethanol also gave N-closure products, the imidazolidinones (IV)[1d,2]; treatment of

---

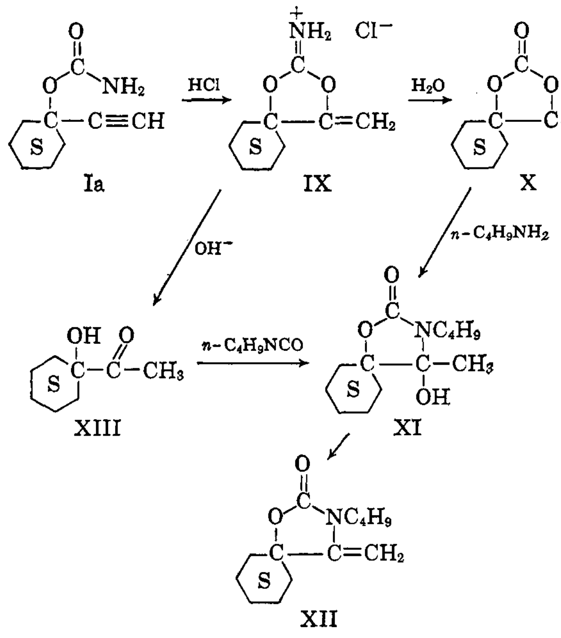
(1) (a) N. R. Easton, D. R. Cassady, and R. D. Dillard, *J. Org. Chem.*, **27**, 2927 (1962); (b) M. D. Cameron, U. S. Patent 2,844,590 (1958); (c) K. Sisido, K. Hukuoka, M. Tuda, and H. Nozaki, *J. Org. Chem.*, **27**, 2663 (1962); (d) N. Shachat and J. J. Bagnell, Jr., *ibid.*, **28**, 991 (1963).

(2) N. R. Easton, D. R. Cassady, and R. D. Dillard, *ibid.*, **29**, 1851 (1964).

the ureas, however, with dry hydrogen chloride in ether precipitated the 2-aminooxazolinium chlorides (V). These salts, upon neutralization with base, gave the 2-iminooxazolidines.[2] This oxygen closure of the ureas was in agreement with the finding that N-acyl derivatives of α,α-disubstituted propargylamines (VII) gave five-membered ring products (VIII) upon treatment with dry hydrogen chloride.[3]



Since the base-induced cyclization of the ureas gave an N-closure, and the acid-catalyzed reaction produced an O-closure, an acid-catalyzed cyclization of the urethanes would be expected to give the O-closure. Treatment of an ether solution of a urethane, 1-ethynylcyclohexyl carbamate (Ia), with dry hydrogen chloride gave a hygroscopic precipitate. When this solid was dissolved in water, an oil was formed. Analyses of this oil showed it to be a nitrogen-free compound. The infrared spectrum ($CHCl_3$) had bands at 5.42, 5.49, 5.82, and 5.93 μ. The n.m.r.[4] spectrum showed, in addition to peaks for the cyclohexane ring, doublets centered at 258 and 284 c.p.s. (2H, J = 3 c.p.s.). These data fit the dioxolane structure (X). An examination of the ether-insoluble solid (isolated under anhydrous conditions) showed it to be the 2-iminodioxolane hydrochloride (IX). Treatment of this iminodioxolane hydrochloride with dilute base liberated the keto alcohol XIII.



Additional proof of structure was obtained by the facile formation of the oxazolidinone (XII) when the dioxolane (X) was treated with n-butylamine. This reaction proceeded through the intermediate hydroxy compound (XI). The methylene oxazolidinone was identical with that formed by the reaction of n-butyl isocyanate upon 1-acetylcyclohexanol (XIII).

In order to test the generality of this reaction, several other urethanes were subjected to this treatment and they formed similar products.

Since the completion of this work, compounds of this type have been reported.[5] They were prepared by the reaction of the t-ethynylcarbinols with carbon dioxide in the presence of a copper salt as catalyst.

Experimental

All melting points were taken in an open capillary using a Culatti electrically heated air bath melting point apparatus.

2-Imino-4,4-pentamethylene-5-methylenedioxolane.—A solution of 10 g. (0.06 mole) of 1-ethynylcyclohexyl carbamate in 200 ml. of ether was saturated with dry hydrogen chloride until precipitation was complete. The solid was removed by filtration under nitrogen. The n.m.r spectrum of the dried material was compatible with the proposed structure.

Anal. Calcd. for $C_9H_{14}ClNO_2$: N, 6.90. Found: N, 6.75.

Owing to the hygroscopic nature of the solid, it was used immediately in the next reaction.

4,4-Pentamethylene-5-methylene-2-dioxolanone.—The crude product from the above reaction was added to 25 ml. of water and the resulting oil, extracted into ether and distilled, had b.p. 60° (2 mm.), yield 8 g. (79% based upon 1-ethynylcyclohexyl carbamate).

Anal. Calcd. for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.45; H, 7.28.

This compound was also prepared by the same route from 1-ethynylcyclohexyl-N-ethyl carbamate (yield 92%).

4,4-Dimethyl-5-methylene-2-dioxolanone.—By the above procedure N-ethyl-2-(2-methyl-3-butynyl) carbamate and N-(4-chlorophenyl)-2-(2-methyl-3-butynyl) carbamate were converted to 4,4-dimethyl-5-methylene-2-dioxolanone, b.p. 35° (10 mm.).

Anal. Calcd. for $C_6H_8O_3$: C, 56.24; H, 6.29. Found: C, 56.35; H, 6.38.

3-*n*-Butyl-4-methylene-5,5-pentamethylene-2-oxazolidinone. Method A.—Twenty-five millimoles (4.2 g.) of the dioxolane was dissolved in 50 ml. of n-butylamine. When the reaction had subsided and returned to room temperature, the excess amine was

---

[3] (a) N. R. Easton, R. D. Dillard, M. Livezey, D. E. Morrison, and G. F. Hennion, Abstracts, 138th National Meeting of the American Chemical Society, New York, N. Y., Sept., 1960, p. 44-O; (b) N. R. Easton and R. D. Dillard, *J. Org. Chem.*, **28**, 2465 (1963).

[4] The machine used was the Varian Associates Model HR60, 60 Mc. Deuteriochloroform was used as the solvent and tetramethylsilane as the internal standard.

[5] Badische Anilin, German Patents 1,098,953 (1961) and 1,145,632 (1963).

removed by vacuum distillation. The resulting solid, m.p. 105–106°, was identified as 3-*n*-butyl-4-hydroxy-4-methyl-5,5-pentamethylene-2-oxazolidinone.

The infrared spectrum showed characteristic peaks at 3.00 and 5.77 μ for the $-OH$ and cyclic urethane carbonyl.

Anal. Calcd. for $C_{13}H_{23}NO_3$: C, 64.70; H, 9.61; N, 5.80. Found: C, 64.54; H, 9.48; N, 5.54.

The hydroxy compound was dehydrated by refluxing a benzene solution under a Dean–Stark trap. Vacuum removal of the solvent yielded an oil, b.p. 165° at 2 mm., yield 4.0 g. (72%).

Anal. Calcd. for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48; N, 6.27. Found: C, 69.85; H, 9.46; N, 6.25.

Method B.—Equal quantities (25 g.) of 1-acetylcyclohexanol and *n*-butyl isocyanate were dissolved in ether. The mixture was cooled in ice due to spontaneous exothermic reaction. Vacuum removal of the solvents yielded the hydroxymethyl oxazolidinone, m.p. 105–106°, identical with that obtained from the dioxolanone.

Treatment of 2-Imino-4,4-pentamethylene-5-methylenedioxolane with Aqueous Sodium Hydroxide.—A sample of the crude 2-iminodioxolane (IX) was dissolved in 10% sodium hydroxide solution. The resulting mixture was extracted with ether. The ether was removed at reduced pressure and the 1-acetyl-1-cyclohexanol distilled, b.p. 105–107° (26 mm.), n^{25}_{D} 1.4660.[6]

Acknowledgment.—The microanalyses were performed by Messrs. William Brown, Howard Hunter, George Maciak, David Cline, and Alfred Brown. Many of the starting materials were prepared in this laboratory by Mr. Lawrence White. The infrared and n.m.r. spectra were obtained by Mr. John Klemm, Mrs. Doris Stephens, and Miss Martha Hofmann. The authors wish to thank especially Dr. Harold Boaz and Messrs. Paul Landis and Donald Woolf, Jr., for their assistance in interpreting the infrared and n.m.r. data.

[6] G. F. Hennion and E. J. Watson, *J. Org. Chem.*, **23**, 656 (1958).

Cannizzaro Reactions Involving Aromatic Dialdehydes[1]

STEWART E. HAZLET, GEORGE BOSMAJIAN, JR.,
JOHN H. ESTES, AND EDWIN F. TALLYN

Department of Chemistry, Washington State University, Pullman, Washington

Received January 16, 1962

An example of a Cannizzaro reaction of an aromatic dialdehyde is on record; Löw[2] found that the reaction of terephthalaldehyde with sodium hydroxide solution yields terephthalic acid, *p*-hydroxymethylbenzoic acid, and α,α′-*p*-xylenediol.

Bromoterephthalaldehyde has now been subjected to Cannizzaro reaction conditions and rather similar results have been observed. The products formed are: the diacid (15% yield), 3-bromo-4-hydroxymethylbenzoic acid (63% yield), and the diol (19% yield); total yield, 97%. The results indicate that the aldehyde function in bromoterephthalaldehyde which is *ortho* to halogen is more easily reduced and that the other aldehyde function is more easily oxidized.

The behavior of mixtures of terephthalaldehyde and formaldehyde and of bromoterephthalaldehyde and formaldehyde in strong sodium hydroxide solution has been studied also. It was found that the extent of reduction of the aromatic dialdehyde to diol increased as the relative amount of formaldehyde was increased. Two examples of these reactions are reported in the Experimental section: (1) a 1:8 terephthalaldehyde to formaldehyde mixture gave 68% yield of α,α′-*p*-xylenediol and 9% yield of *p*-hydroxymethylbenzoic acid; (2) a 1:12 bromoterephthalaldehyde to formaldehyde mixture gave 76% yield of bromo-α,α′-*p*-xylenediol and 22% yield of 3-bromo-4-hydroxymethylbenzoic acid.

Some of the compounds required for use or comparison were prepared by methods which have been described previously (terephthalaldehyde,[2] *p*-hydroxymethylbenzoic acid,[2] and α,α′-*p*-xylenediol[3]) or were available (terephthalic acid, Eastman White Label). Others have now been synthesized, and methods and related data are reported in the Experimental section; derivatives of a number of these compounds have been prepared by standard procedures.

Experimental

Bromoterephthalaldehyde.—Crude α,α,α′,α′-tetrabromobromo-*p*-xylene (100 g., 0.2 mole, from *p*-xylene → bromo-*p*-xylene[4] → α,α,α′,α′-tetrabromobromo-*p*-xylene[5]) and 200 ml. of concentrated sulfuric acid were placed in a flask fitted with a stirrer and attached to a glass aspirator to remove hydrogen bromide and bromine fumes; this was maintained at 140° until no more fumes were evolved (*ca.* 45 min.). The reaction mixture was poured onto crushed ice; after the ice had melted, the mixture was steam distilled. The product weighed 21 g. (49% yield), m.p. 67–68°; further purification by steam distillation or by crystallization from water increased the melting point to 75°.

Anal. Calcd. for $C_8H_5BrO_2$: C, 45.07; H, 2.35; Br, 37.56. Found: C, 44.97; H, 2.54; Br, 37.73.

From the aldehyde, the following compounds were prepared: (a) the **dioxime**, (b) the **tetraacetate**, and (c) **bromoterephthalic acid**.

The dioxime melted at 218° (from ethanol).

Anal. Calcd. for $C_8H_7BrN_2O_2$: Br, 32.92; N, 11.52. Found: Br, 33.25; N, 11.39.

The tetraacetate melted at 132° (from ethanol).

Anal. Calcd. for $C_{16}H_{17}BrO_8$: C, 46.04; H, 4.08; Br, 19.18. Found: C, 46.00; H, 4.27; Br, 18.99.

Bromoterephthalic acid melted at 299° (from water, sublimes), lit.[6] m.p. 299°, neut. equiv. 124.

α,α′-Dibromobromo-*p*-xylene.—To bromo-*p*-xylene[4] (92.5 g., 0.5 mole) bromine (160 g., 1 mole) was added slowly (quartz apparatus; ultraviolet irradiation; oil bath temperature, 130°; reaction time, 2 hr.). Cooling the reaction mixture caused the major portion of it to solidify; recrystallization from ligroin (b.p. 90–120°) gave colorless crystals, 60 g. (35% yield), m.p. 91–92°.

Anal. Calcd. for $C_8H_7Br_3$: Br, 69.97. Found: Br, 69.94.

Bromo-α,α′-*p*-xylenediol.—The above tribromo compound (25 g., 0.0729 mole) was refluxed with 10% potassium carbonate solution. The hot reaction mixture was filtered, and the cooled filtrate was saturated with potassium carbonate. The precipitated diol weighed 5.5 g. (35% yield), m.p. 110–111° (from water).

Anal. Calcd. for $C_8H_9BrO_2$: C, 44.24; H, 4.15; Br, 36.87. Found: C, 44.52; H, 4.43; Br, 36.80.

From the diol, the following compounds were prepared: (a) the **diacetate**, (b) the **dibenzoate**, and (c) the **di-*p*-nitrobenzoate**.

The diacetate melted at 66–67° (from ethanol).

Anal. Calcd. for $C_{12}H_{13}BrO_4$: Br, 26.58. Found: Br, 26.64.

The dibenzoate had a melting point of 98–99° (from ethanol).

Anal. Calcd. for $C_{22}H_{17}BrO_4$: Br, 18.82. Found: Br, 18.82.

The di-*p*-nitrobenzoate melted at 164.5–165.5° (from benzene).

Anal. Calcd. for $C_{22}H_{15}BrN_2O_8$: Br, 15.53; N, 5.44. Found: Br, 15.57; N, 5.24.

α-Bromo-2-bromo-*p*-tolunitrile.—2-Bromo-*p*-tolunitrile (42.5

---

[1] This investigation was supported in part by the Office of Naval Research.

[2] W. Löw, *Ann.*, **231**, 373 (1885).

[3] E. Grimaux, *ibid.*, **155**, 338 (1870).

[4] G. T. Morgan and E. A. Coulson, *J. Chem. Soc.*, 2211 (1929).

[5] By a method analogous to that used by J. M. Snell and A. Weissberger [*Org. Syn.*, **20**, 92 (1940)] for the preparation of α,α,α′,α′-tetrabromo-*p*-xylene.

[6] F. C. Whitmore and L. L. Isenhour, *J. Am. Chem. Soc.*, **51**, 2787 (1929).